Unit VI Free Response

- 2004 Question 3a-b, d-e

The first order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of 5.00 x 10^3 $cm^{-1} \cdot M^{-1}$ and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table below:

[X] (M)	Absorbance	Time (min)
?	0.600	0.0
4.00 x 10^{-5}	0.200	35.0
3.00 x 10^{-5}	0.150	44.2
1.50 x 10^{-5}	0.075	?

(a) Calculate the initial concentration of the colored species.

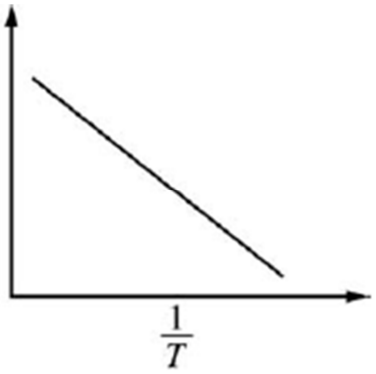
(b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.

(d) Calculate the half-life of the reaction. Include units with your answer.

(e) Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph below, where T is temperature. This graph can be used to determine the activation energy (E_a) of the reaction.

(i) Label the vertical axis of the graph.

(ii) Explain how to calculate the activation energy from this graph.



- 2004 B Question 1

For the reaction represented below, the value of the equilibrium constant (K_p) is 3.1 x 10^{-4} at 700 K:

$$N_2\,(g) + 3\,H_2\,(g) \leftrightarrow 2\,NH_3\,(g)$$

(a) Write the expression for the equilibrium constant (K_p) for the reaction.
(b) Assume that the initial partial pressures of the gases are as follows:

$$P_{N_2} = 0.411\ atm, P_{H_2} = 0.903\ atm, P_{NH_3} = 0.224\ atm$$

(i) Calculate the value of the reaction quotient (Q) at these initial conditions.
(ii) Predict the direction in which the reaction will proceed at 700 K if the initial partial pressures are those given above. Justify your answer.

(c) Calculate the value of the equilibrium constant (K_c), given that the value of K_p for the reaction at 700 K is 3.1×10^{-4}.
(d) The value of K_p for the reaction represented below is 8.3×10^{-3} at 700 K:

$$NH_3\ (g) + H_2S\ (g) \leftrightarrow NH_4HS\ (g)$$

Calculate the value of K_p at 700 K for each of the reactions represented below:

(i) $NH_4HS\ (g) \leftrightarrow NH_3\ (g) + H_2S\ (g)$
(ii) $2\ H_2S\ (g) + 2\ NH_3\ (g) \leftrightarrow 2\ NH_4HS\ (g)$

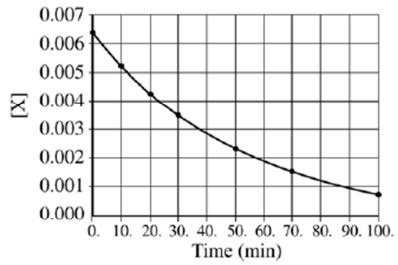
- 2005 B Question 3

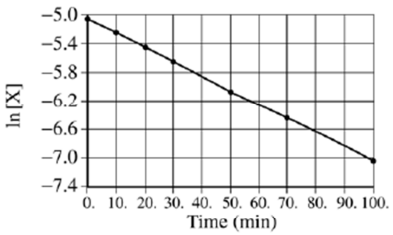
The decomposition of gas X to produce gases Y and Z is represented by the equation below:

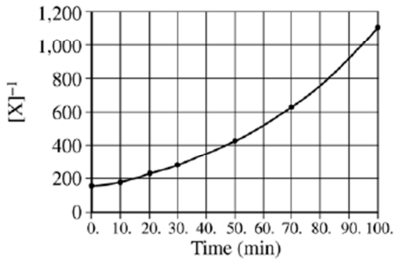
$$X \leftrightarrow 2\ Y + Z$$

In a certain experiment, the reaction took place in a 5.00 L flask at 428 K. Data from this experiment were used to produce the information in the table below, which is plated in the graphs below that:

Time (minutes)	**[X] (M)**	**ln [X]**	**$[X]^{-1}$ (M^{-1})**
0	0.00633	-5.062	158
10	0.00520	-5.259	192
20	0.00427	-5.456	234
30	0.00349	-5.658	287
50	0.00236	-6.049	424
70	0.00160	-6.438	625
100	0.000900	-7.013	1,110







(a) How many moles of X were initially in the flask?
(b) How many molecules of Y were produced in the first 20 minutes of the reaction?
(c) What is the order of this reaction with respect to X? Justify your answer.
(d) Write the rate law for this reaction.
(e) Calculate the specific rate constant for this reaction. Specify units.
(f) Calculate the concentration of X in the flask after a total of 150 minutes of reaction.

- 2005 Question 3

Iodide ion (I^-) is oxidized to hypoiodite ion (IO^-) by hypochlorite (ClO^-) in basic solution according to the equation below:

$$I^-(aq) + ClO^-(aq) \xrightarrow{OH^-} IO^-(aq) + Cl^-(aq)$$

Three initial-rate experiments were conducted; the results are shown in the following table:

Experiment	$[I^-]$ (M)	$[ClO^-]$ (M)	Initial Rate (M/s)
1	0.017	0.015	0.156
2	0.052	0.015	0.476
3	0.016	0.061	0.596

(a) Determine the order of the reaction with respect to each reactant listed below. Show your work.
  (i) I^- (aq)
  (ii) ClO^- (aq)
(b) For the reaction,
  (i) write the rate law that is consistent with the calculations in part a
  (ii) calculate the value of the specific rate constant (k) and specify unit.

The catalyzed decomposition of hydrogen peroxide (H_2O_2) is represented by the following equation:

$$2\ H_2O_2\ (aq) \xrightarrow{catalyst} 2\ H_2O\ (l) + \ O_2\ (g)$$

The kinetics of the decomposition reaction were studied and the analysis of the results show that it is a first-order reaction. Some of the experimental data are shown in the table below:

[H_2O_2] (M)	**Time (minutes)**
1.00	0.0
0.78	5.0
0.61	10.0

(c) During the analysis of the data, the graph below was produced.

(i) Label the vertical axis of the graph.

(ii) On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 M H_2O_2.

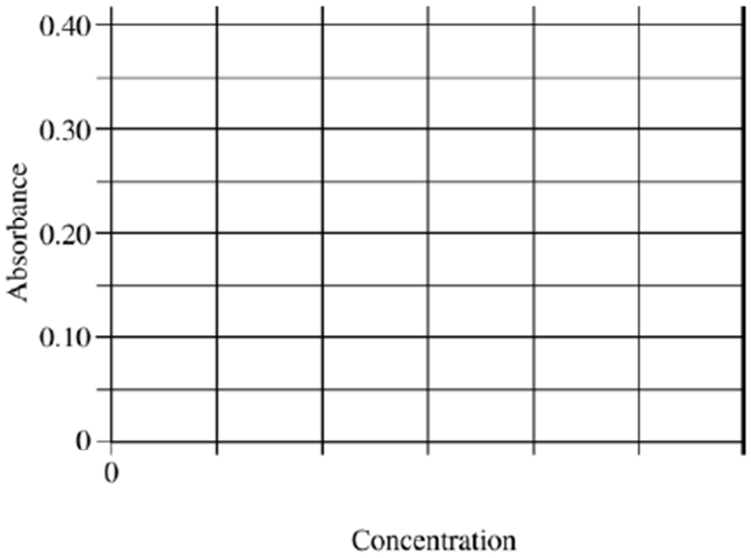
- 2006 B Question 5b-d

A student carries out an experiment to determine the equilibrium constant for a reaction by colorimetric (spectrophotometric) analysis. The production of the red-colored species $FeSCN^{2+}$ is monitored.

(b) A calibration plot for the concentration of $FeSCN^{2+}$ is prepared at the optimum wavelength. The data below give the absorbances measured for a set of solutions of known concentrations of $FeSCN^{2+}$.

Concentration (M)	**Absorbance**
1.1×10^{-4}	0.030
3.0×10^{-4}	0.065
8.0×10^{-4}	0.160
12×10^{-4}	0.239
18×10^{-4}	0.340

(i) Draw a Beer's law calibration plot of all the data on the grid below. Indicate the scale on the horizontal axis by labeling it with appropriate values.



(ii) A $FeSCN^{2+}$ solution of unknown concentration has an absorbance of 0.300. Use the plot in part i to determine the concentration, in moles per liter, of this solution.

(c) The purpose of the experiment is to determine the equilibrium constant for the reaction represented below:

$$Fe^{3+}\ (aq) + SCN^{-}\ (aq) \leftrightarrow FeSCN^{2+}\ (aq)$$

(i) Write the equilibrium constant expression for K_c.

(ii) The student combines solutions of $Fe(NO_3)_3$ and KSCN to produce a solution in which the initial concentrations of Fe^{3+} and SCN^- are both 6.0×10^{-3} M. The absorbance of this solution is measured and the equilibrium $FeSCN^{2+}$ concentration is found to be 1.0×10^{-3} M. Determine the value of K_c.

(d) If the student's equilibrium $FeSCN^{2+}$ solution of unknown concentration fades to a lighter color before the student measures its absorbance, will the calculated value of K_c be too high, too low or unaffected? Justify your answer.

- 2009 Question 3d-e

Methane gas reacts with chlorine gas to form dichloromethane and hydrogen chloride, as represented by the equation below:

$$CH_4\ (g) + 2\ Cl_2\ (g) \leftrightarrow CH_2Cl_2\ (g) + 2\ HCl\ (g)$$

The following mechanism has been proposed for the reaction of methane gas with chlorine gas. All species are in the gas phase.

Step 1	$Cl_2 \leftrightarrow 2\ Cl$	*fast equilibrium*
Step 2	$CH_4 + Cl \leftrightarrow CH_3 + HCl$	*slow*
Step 3	$CH_3 + Cl_2 \leftrightarrow CH_3Cl + Cl$	*fast*
Step 4	$CH_3Cl + Cl \leftrightarrow CH_2Cl_2 + H$	*fast*

Step 5 $H + Cl \leftrightarrow HCl$ *fast*

(d) In the mechanism, is CH_3Cl a catalyst, or is it an intermediate? Justify your answer.

(e) Identify the order of the reaction with respect to each of the following according to the mechanism. In each case, justify your answer.

(i) CH_4

(ii) Cl_2